



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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**Published**

*With international search report.*

*With amended claims.*

(54) Title: COPPER AMINE FUNGICIDAL COMPOSITION

## (57) Abstract

Aqueous colloidal suspensions comprising 2 moles of ammonia per mole of cupric salt are effective broad-spectrum fungicides for protecting plants from fungi and for combatting fungi infesting plants. They are readily applied to plant foliage by spraying or fumigation.

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## COPPER AMINE FUNGICIDAL COMPOSITION

### Field of the Invention

Copper amine complexes are effective to protect plants from fungi or to combat fungi on fungi-infested plants.

### Background

The fungicidal properties of copper salts have been known for many years, but phytotoxicity precluded widespread use of such salts until Milardet (1882) discovered that, by adding lime, copper sulfate was made safe (called safening), as an insoluble colloidal suspension of copper calcium sulfate and hydroxide, Bordeaux mixture, was formed.

This colloidal suspension, when sprayed on foliage, covers leaves with a film, which gradually produces toxic-to-fungi soluble copper.

Realizing that it was the gradual production of soluble copper that diminished phytotoxicity of fungicides based on copper, many copper compounds were developed that were less phytotoxic than Bordeaux mixture, such as copper silicate, copper zeolite, cuprous oxide, copper oxychloride, copper carbonate, and others which, with the humidity and carbon dioxide of the atmosphere, slowly release soluble copper at concentrations effectively toxic to fungi but not to plants.

Unfortunately, the slow release of cupric ions from such compounds requires a large amount of fungicide, which flower growers object to since it stains the leaves and flowers; grape and strawberry growers also have this problem in addition to copper accumulation on the soil.

### Summary of the Invention

In order to solve these problems, a series of experiments was carried out using copper complexes as biocides. Instead of cupric ions, ethylene diamine tetra acetate (EDTA), citrate, E H P G and amines were tried. A copper diamine complex was found to be more toxic to fungi than copper ions and less phytotoxic than the other copper compounds described above, both in the laboratory and in

field testing.

Surprisingly, the doses of the copper diamine complex required for complete control are about one tenth of that needed with other copper fungicides. The copper diamine complex is adsorbed by leaves through cuticle and remains in inner spongy tissue, thus attacking both the aerial hyphae and the mycelium of fungi established in the spongy tissue. Retention of copper diamine in the spongy tissue provides residuality which is lost with other copper fungicides, which, e.g., in case of rain, not being protected by the cuticle, are washed away.

An object of this invention is to provide an effective, but substantially non-phytotoxic fungicide for protecting plants as well as for combatting fungi on plants infested thereby. A further object is to provide a copper-based fungicide which is effective with a significantly-reduced amount of copper. Another object is to provide a copper-based fungicide which is adsorbed by plant leaves and remains in inner spongy leaf tissue. A still further object is to provide a broad-spectrum fungicide, suitable for application to a large variety of plants. Still further objects are apparent from the following description.

There are a number of different aspects of the invention, as follows:

1. An aqueous colloidal suspension of a cupric salt and ammonia comprising 2 moles of ammonia per mole of cupric salt;
2. A substantially non-phytotoxic fungicidal composition based on the aqueous colloidal suspension of (1);
3. A fungicidal composition (2) wherein the cupric salt is copper nitrate;
4. A method of protecting plants from fungi or for combatting fungi on plants which comprises spraying foliage of the plants with a fungicidal composition (2).

#### Details:

An aqueous suspension of copper amine salt complex is a broad-spectrum fungicide suitable for combatting fungi on plants as well as for protecting plants from attack by fungi. In the example

(which follows) copper diamine nitrate is used. Although the nitrate additionally acts as a foliar fertilizer, other salts, such as the sulfate or chloride, can be similarly used to produce effective fungicides. The particular cupric salt selected is not critical.

#### Example

800cc of aqueous cupric nitrate solution containing two moles of cupric nitrate are mixed with 200cc of ammonia water containing four moles of ammonia. The thus-formed colloidal suspension (The Suspension), when diluted ten times with water, is neutral (has a pH of 7 and 2 moles of copper nitrate per 10 liters of suspension).

This fungicide is effective for treating a broad spectrum of fungi in plants. For treating potato plants infested with Alternaria, 1.0cc of The Suspension per liter of water is effective. For fumigating over an extensive area, from 400 to 800cc of The Suspension (diluted in the proportion of 1cc of The Suspension per liter of water) are used to fumigate each hectare. For treating tomato plants infested with Cladosporium fulvum, similar dosing is effective. For treating strawberries infested with Botrytis, however, from 0.5 to 1cc of The Suspension (diluted in the proportion of 1cc of The Suspension per liter of water) is effective; this corresponds to from 200 to 400cc of The Suspension (similarly diluted) per hectare (by fumigation).

Copper fungicides are distinctly advantageous for treating plants because of their low toxicity to humans. The limit of toxicological tolerance for copper in man is so high that no problem arises in its use for parasite control on crops. Copper salts have actually been used for this purpose for more than fifty years.

The invention and its advantages will be readily understood from the preceding description. Various changes may naturally be made in the compositions and methods without departing from the spirit and scope of the invention or sacrificing its material advantages. The processes and compositions described herein are merely illustrative of preferred embodiments of the invention.

WHAT IS CLAIMED IS:

1. An aqueous colloidal suspension of a cupric salt and ammonia comprising 2 moles of ammonia per mole of cupric salt.
2. An aqueous suspension of claim 1 wherein the copper and ammonia are in the form of a copper amine complex.
3. A substantially non-phytotoxic fungicidal composition which consists essentially of a suspension of claim 1.
4. A fungicidal composition of claim 3 wherein the cupric salt is copper nitrate.
5. A fungicidal composition of claim 3 wherein the cupric salt is copper sulfate.
6. A fungicidal composition of claim 3 wherein the cupric salt is copper chloride.
7. A fungicidal composition of claim 3 comprising about 2 moles of copper per liter.
8. A fungicidal composition of claim 3 comprising about 0.2 mole of copper per liter and having a pH of about 7.
9. A fungicidal composition of claim 3 comprising about 0.002 mole of copper per liter.
10. A method of protecting plants from fungi or for combatting fungi on plants which comprises spraying foliage of the plants with a composition of claim 3.
11. A method of claim 10 wherein the fungi are Alternaria, Cladosporium fulvum or Botrytis.

12. A method of claim 10 wherein the plants are potato, tomato or strawberry.

13. A method of protecting plants from fungi or for combatting fungi on plants which comprises spraying foliage of the plants with an aqueous colloidal suspension of copper amine complex.

14. A method of claim 13 wherein the copper amine complex is that of a copper salt selected from the group consisting of copper nitrate, copper sulfate and copper chloride.

## AMENDED CLAIMS

[received by the International Bureau on 08 February 1996 (08.02.96);  
original claim 11 amended;  
remaining claims unchanged (2 pages)]

1. An aqueous colloidal suspension of a cupric salt and ammonia comprising 2 moles of ammonia per mole of cupric salt.

2. An aqueous suspension of claim 1 wherein the copper and ammonia are in the form of a copper amine complex.

3. A substantially non-phytotoxic fungicidal composition which consists essentially of a suspension of claim 1.

4. A fungicidal composition of claim 3 wherein the cupric salt is copper nitrate.

5. A fungicidal composition of claim 3 wherein the cupric salt is copper sulfate.

6. A fungicidal composition of claim 3 wherein the cupric salt is copper chloride.

7. A fungicidal composition of claim 3 comprising about 2 moles of copper per liter.

8. A fungicidal composition of claim 3 comprising about 0.2 mole of copper per liter and having a pH of about 7.

9. A fungicidal composition of claim 3 comprising about 0.002 mole of copper per liter.

10. A method of protecting plants from fungi or for combatting fungi on plants which comprises spraying foliage of the plants with a composition of claim 3.

11. A method of claim 10 wherein the fungi are *Alternaria*, *Cladosporium fulvum* or *Botrytis*.



12. A method of claim 10 wherein the plants are potato, tomato or strawberry.

13. A method of protecting plants from fungi or for combatting fungi on plants which comprises spraying foliage of the plants with an aqueous colloidal suspension of copper amine complex.

14. A method of claim 13 wherein the copper amine complex is that of a copper salt selected from the group consisting of copper nitrate, copper sulfate and copper chloride.

## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/11673

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 424/630, 632-638, 718, 719, 721; 514/951, 952; 71/Dig. 1; 504/101.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN, Files CA &amp; CABA. Search Terms: (cupric or copper) (2w) hydroxide; (pesticide? or fungicide?); (suspension? or colloid?); bordeaux.

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Proc. 45th N.Z. Plant Protection Conf., issued 1992, Olson et al., "Control of Alternaria and Melanose on citrus using chlorothalonil and cupric hydroxide," pages 95-98, in particular, page 95, last paragraph.	1-14
Y	Kidd et al, "The Agrochemicals Handbook", 3rd ed., published August 1991, (Cambridge, GB), see page A0460.	1-14
Y	Sine et al. (eds.), "Farm Chemicals Handbook '87," published 1987 by Meister Publishing Co. (Ohio), see pages C67, C68, C69, C70, B19, B21.	1-14



Further documents are listed in the continuation of Box C.



See patent family annex.

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Date of the actual completion of the international search

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## INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US95/11673

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	DE, A, 3,145,997 (NORDDEUT AFFINERIE AG) 01 June 1983, see entire document, especially pages 1 and 5, English translation enclosed.	1-14
Y	AU, A, 15,856 (STANCO INC.) 22 November 1934, see entire document, especially column 1, lines 19-20 & 24-28.	1-14
Y	US, A, 4,125,393 (KOHL et al.) 14 November 1978, see entire document, especially column 1, lines 10-16 and column 5, lines 48-55.	1-14

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**A. CLASSIFICATION OF SUBJECT MATTER:**

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424/630, 632-638, 718, 719, 721; 514/951, 952; 71/Dig. 1; 504/101.